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(54) Title: OXIDATIVE HALOGENATION OF C_1 HYDROCARBONS TO HALOGENATED C_1 HYDROCARBONS AND INTEGRATED PROCESSES RELATED THERETO

(57) Abstract: An oxidative halogenation process involving contacting a reactant hydrocarbon selected from methane, a halogenated C_1 hydrocarbon, or a mixture thereof with a source of halogen and, preferably, a source of oxygen in the presence of a rare earth halide or rare earth oxyhalide catalyst, so as to form a halogenated C_1 hydrocarbon having a greater number of halogen substituents as compared with the reactant hydrocarbon. Preferably, the product is a monohalogenated methane, more preferably, methyl chloride. The oxidative halogenation process to form methyl halide can be integrated with downstream processes to produce valuable commodity chemicals, for example, methyl alcohol and/or dimethyl ether; light olefins, including ethylene, propylene, and butenes; higher hydrocarbons, including gasolines; vinyl halide monomer, and acetic acid. Hydrogen halide, which is a co-product of these downstream processes, can be recycled to the oxidative halogenation process.

OXIDATIVE HALOGENATION OF C_1 HYDROCARBONS TO HALOGENATED C_1 HYDROCARBONS AND INTEGRATED PROCESSES RELATED THERETO

In a first aspect, this invention pertains to a process for the oxidative halogenation of methane or halogenated C_1 hydrocarbons. For the purposes of this discussion, the term "oxidative halogenation" shall refer to a process wherein methane or a halogenated C_1 hydrocarbon (the "reactant hydrocarbon") is contacted with a source of halogen and, optionally, a source of oxygen so as to form a halogenated C_1 hydrocarbon having a greater number of halogen substituents as compared with the reactant hydrocarbon. The oxidative chlorination of methane with hydrogen chloride in the presence of oxygen to form methyl chloride is an example of this process.

Monohalogenated methanes, such as methyl chloride, find utility in the production of silicones and higher halogenated methanes and can also be used as intermediates in the production of numerous commodity chemicals, for example, methanol, dimethyl ether, light olefins, including ethylene and propylene, and higher hydrocarbons, such as gasolines. Other halogenated C_1 hydrocarbons, such as dichloromethane, find utility as solvents, as intermediates for the manufacture of silicones, and in the methylation or etherification of cellulose, alcohols, and phenols, for example.

In a second aspect, this invention pertains to a process of preparing methyl alcohol and/or dimethyl ether by way of the oxidative halogenation of methane to form methyl halide and thereafter the hydrolysis of methyl halide to form methanol and/or dimethyl ether. Both methanol and dimethyl ether can be used as components in gasolines. Methanol, itself, can be used as a motor fuel, as a source of energy, and as a raw material feedstock for a variety of useful syntheses.

In a third aspect, this invention pertains to a process of preparing light olefins, such as ethylene, propylene, and butenes, and/or heavier hydrocarbons, such as C5+ gasolines, by way of the oxidative halogenation of methane to form methyl halide and the subsequent condensation of methyl halide to form light olefins and/or gasolines. Light olefins, such as ethylene, propylene, and butenes, are used as monomers in the production of poly(olefins), such as poly(ethylene), poly(propylene) and poly(butadienes), as well as being used as feedstocks for many valuable chemicals, for example, styrene, vinyl chloride monomer, cumene, and butadiene. The utility of gasolines is well known.

In a fourth aspect, this invention pertains to a process of preparing vinyl halide monomer using methane as a raw material. Vinyl halide monomer finds utility in the manufacture of poly(vinyl halide) polymers, notably poly(vinyl chloride).

In a fifth aspect, this invention pertains to a process of preparing acetic acid using methane as a raw material. Acetic acid finds wide utility in the manufacture of vinyl acetate and cellulose acetate, and in the production of important solvents, such as ethyl acetate, n-butyl acetate, isobutyl acetate, and methyl acetate.

As ready supplies and access to crude oil have become more uncertain, alternative sources of hydrocarbons and fuel have been sought out and explored. The conversion of natural gas, containing predominantly low molecular weight alkanes, to higher molecular weight hydrocarbons has received increasing consideration, as natural gas is generally available from readily secured and reliable sources. Large deposits of natural gas, chiefly composed of methane, are found in many locations throughout the world. In addition, low molecular weight alkanes are generally present in coal deposits and can be formed during mining operations, in various petroleum processes, and in the gasification or liquefaction of synthetic fuelstocks, such as, coal, tar sands, oil shale, and biomass. Moreover, in the search for petroleum, large amounts of natural gas are often discovered in remote parts of the world, such as remote parts of Western Canada, Australia, China, and the former Soviet Union, where there are no local markets for the use of natural gas as a fuel or as a chemical feedstock.

Much of the readily accessible natural gas is used in local markets as fuel in residential, commercial, and industrial applications. Typically, materials used as fuel are traded at prices below the prices commanded for chemical feedstocks. Use of natural gas as a chemical feedstock is, thus, a high-value application. Accessibility, however, is a major obstacle to the effective and extensive use of remote gas, whether for fuel or feedstock. In fact, vast quantities of natural gas are often flared, particularly in remote areas from which its transport in gaseous form is practically impossible.

Conversion of natural gas to useful chemical feedstocks, preferably liquid feedstocks, offers a promising solution to the problem of transporting low molecular weight hydrocarbons from remote locations; but conversions of this sort present a special challenge to the petrochemical and energy industries. The dominant technology now employed for utilizing remote natural gas involves its conversion to synthesis gas, also commonly referred

to as "syngas," a mixture of hydrogen and carbon monoxide, with the syngas subsequently being converted to liquid products. Synthesis gas can be converted to syncrude, such as, with Fischer-Tropsch technology, and syncrude can then be upgraded to transportation fuels using typical refining methods. Alternatively, synthesis gas can be converted to liquid oxygenates, such as methanol, which in turn can be converted to more conventional transportation fuels via certain zeolitic catalysts.

While syngas processing provides a means for converting natural gas into a more easily transportable liquid that in turn can be converted into useful chemical products, the intermediate step involved in such processing, i.e., the formation of the synthesis gas, is disadvantageously costly. The cost occurs in adding oxygen to the substantially inert methane molecule to form the syngas mixture of hydrogen and carbon monoxide, and occurs again in removing the oxygen when hydrocarbons are the desired end-product. As a further disadvantage, if synthesis gas is to be used to make methanol or hydrocarbon products, the syngas should be made at high pressure and high temperature to achieve acceptable syngas formation rates. Accordingly, a search continues for alternate means of converting methane directly to more valuable chemical feedstocks.

A potential alternate route to activating methane involves its oxidative halogenation in a first step to form methyl halide or other lower halogenated methanes, for example, dihalomethanes, which can then be converted in a second step into valuable commodity chemicals, such as methanol, dimethyl ether, light olefins, and higher hydrocarbons, including gasoline. When applied to chlorine halogenation, this route has been referred to as the "chlorine-assisted" route, which can be represented by the following two-step process (I) and (II):

$$CH_4 + HCl + O_2 \rightarrow \text{chloromethane(s)} + H_2O \qquad \text{(I)}$$

$$\text{chloromethane(s)} \rightarrow \text{chemical product} + HCl \qquad \text{(II)}$$

For such a reaction scheme to be practical, the HCl generated in the second step should be efficiently recycled to the first step of the process.

Numerous references describe the catalyzed oxidative halogenation of methane to halogenated methanes, as noted, for example, in the following representative art: US 3,172,915, US 3,657,367, US 4,769,504, and US 4,795,843. Catalysts for the oxidative halogenation of hydrocarbons, such as methane, have typically consisted of first row

transition metal halides, particularly, copper chloride, with promoters, such as potassium and lanthanum chlorides, supported on silica or alumina. Other common catalysts include iron compounds or cerium oxide, optionally, with one or more alkali or alkaline earth metal chlorides, and/or optionally, with one or more rare earth compounds, supported on an inert carrier, typically alumina, silica, or an aluminosilicate.

Disadvantageously, the oxidative halogenation processes cited hereinabove produce an unacceptable quantity of perhalogenated product, such as carbon tetrachloride, which is less valuable than lower halogenated products, such as methyl chloride and dichloromethane. As a further disadvantage, the prior art processes produce an unacceptable quantity of deep oxidation products (CO_x), specifically, carbon monoxide and carbon dioxide. The production of lower value perhalogenated products and undesirable oxidized products irretrievably wastes the C_1 hydrocarbon feed and creates product separation and by-product disposal problems. As a further disadvantage, many of the transition metal halides, used as catalysts, exhibit significant vapor pressure at reaction temperatures; that is, these catalysts are volatile. The volatility generally produces a decline in catalyst activity and/or deposition of corrosive materials in downstream parts of the process equipment.

It is also known to monohalogenate methane with elemental halogen over supported acid or platinum metal catalysts to methyl halide and halogen acid, as disclosed, for example, in US 4,523,040 and US 5,354,916. The supported acid catalysts are disclosed to include ferric oxychloride, tantalum oxyfluoride, niobium oxyfluoride, zirconium oxyfluoride, and antimony oxyfluoride, supported on alumina. Disadvantageously, these prior art catalysts exhibit reaction rates and lifetimes that are too low for practical use. As a further disadvantage, the halogen acid formed must be converted back to elemental halogen and water, which makes the process uneconomical for most applications.

Pertaining to the second aspect of this invention, it is known to oxyhalogenate methane to methyl chloride and thereafter to hydrolyze methyl chloride to methyl alcohol and dimethyl ether, as illustrated, for example, by US 1,086,381, US 4,523,040, and US 5,243,098. Conventional copper halide and platinum halide catalysts are disclosed for the oxyhalogenation step; zinc and magnesium oxides are disclosed for catalyzing the hydrolysis.

Pertaining to the third aspect of this invention, one skilled in the art knows that the current method of obtaining ethylene involves the steam cracking of ethane. Steam crackers are disadvantageously costly, complex, and energy intensive units that must be located at the site of oil refineries. More disadvantageously, steam-cracking produces complex mixtures of cracking products and hydrogen, which must undergo extensive and costly separations and purifications to obtain pure ethylene. In contrast, the synthesis of ethylene from methane via intermediate methyl halide should employ simpler engineering and less complex and less costly separations. In a related aspect, higher hydrocarbons, such as diesel oils and gasolines, can be manufactured via Fischer-Tropsch syntheses that require a syngas plant and complex separations operations of the Fischer-Tropsch product mixtures. Again, the route from methane to gasoline via intermediate methyl chloride should eliminate the need for a syngas plant and would greatly simplify separation efforts. Various patents disclose the condensation of methyl halides to light olefins and/or higher hydrocarbons, including, for example, US 3,894,107, US 5,087,786, and US 5,397,560.

In addition to the above, US 4,737,594 discloses a process for the manufacture of vinyl chloride involving the condensation of methyl chloride, obtained from methane, followed by oxychlorination of the condensation products, and then dehydrochlorination to vinyl chloride. The condensation step is taught to be carried out in the presence of a bifunctional catalyst, preferably, the oxides, oxyhalides, or sulfides of the transition metals of Groups IV, V, VI and VII of the Periodic Table. The oxychlorination is taught to be conducted in the presence of conventional copper chloride catalysts; while the dehydrochlorination is purely thermal.

The art also discloses preparing acetic acid via the oxidation of acetaldehyde, via alkane/alkene oxidations, via carbonylation of methanol, and via the conversion of synthesis gas, as discussed, for example, by K. Weissermel and H.-J. Arpe in *Industrial Organic Chemistry*, 2nd ed., VCH Verlagsgesellschaft mbH, Germany, 1993, pp. 168-175. This art appears to be silent, however, with respect to preparing acetic acid starting from methane, but without the use of methanol intermediate.

The use of halogen-assisted C_1 chemistry, based on methane as a raw material, for the preparation of the above-identified commodity chemicals will strongly depend upon halogenating methane with acceptable selectivity to methyl halide and, optionally, dichloromethane. Since the direct halogenation of methane with elemental halogen is

substantially non-selective for methyl halide, and since the catalytic oxidative halogenation of methane is either non-selective for methyl halide or impractical, the current method of preparing methyl chloride, for example, depends on the reaction of methanol with hydrochloric acid. Accordingly, if C_1 chemistry based on the oxidative halogenation of methane to methyl halide and other lower halogenated methanes is to advance, then various improvements in prior art processes will be required. Specifically, an increase in selectivity to monohalogenated C_1 hydrocarbon is needed. Likewise, a reduction in selectivities to perhalogenated C_1 product and oxygenated products is needed. An increase in catalyst activity and catalyst lifetime are also needed. With these improvements, the conversion of C_1 hydrocarbons, particularly methane, to halogenated C_1 hydrocarbons, particularly methyl halide, will be more attractive. Likewise, downstream applications, particularly, of monohalogenated methyl halides to methanol, dimethyl ether, vinyl halide monomer, acetic acid, light olefins, and higher hydrocarbons, including gasoline, will also be more attractive, thereby increasing the overall value of methane-based C_1 chemistry.

In one aspect, this invention provides for a novel oxidative halogenation process for preparing halogenated C_1 hydrocarbons. The novel process of this invention comprises contacting methane, a halogenated C_1 hydrocarbon, or a mixture thereof, the aforementioned compound(s) being referred to in various places hereinafter as the "reactant hydrocarbon," with a source of halogen and, optionally, a source of oxygen in the presence of a catalyst under process conditions sufficient to prepare a halogenated C_1 hydrocarbon product having a greater number of halogen substituents as compared with the reactant hydrocarbon. The catalyst used in the process of this invention comprises a rare earth halide or rare earth oxyhalide substantially free of copper and iron, with the proviso that when cerium is present in the catalyst, at least one other rare earth element is also present in the catalyst.

The novel oxidative halogenation process of this invention advantageously converts methane or a halogenated C_1 hydrocarbon, such as methyl chloride, in the presence of a source of halogen and, optionally, a source of oxygen into a halogenated C_1 hydrocarbon product having an increased number of halogen substituents as compared with the reactant hydrocarbon, i.e., methane or the reactant halogenated C_1 hydrocarbon, as the case may be. In this process, the use of a source of oxygen is preferred. In another preferred embodiment, the process of this invention can be beneficially employed to oxidatively chlorinate methane in the presence of hydrogen chloride and oxygen to form methyl chloride. Methyl chloride

is beneficially employed in the preparation of methanol, dimethyl ether, light olefins, such as ethylene, propylene, and butenes, and higher hydrocarbons, including gasolines. As compared with prior art processes, the process of this invention advantageously produces the halogenated C_1 hydrocarbon in high selectivity with essentially no perhalogenated C_1 halocarbon, such as carbon tetrachloride, and low levels, if any, of undesirable oxygenates, such as, carbon monoxide and carbon dioxide. The lower selectivity to perhalogenated C_1 halocarbons and undesirable oxygenated by-products correlates with a more efficient use of reactant hydrocarbon, a higher productivity of the desired halogenated C_1 hydrocarbon product, and fewer separation and waste disposal problems.

In addition to the above advantages, the catalyst employed in the process of this invention does not require a conventional carrier or support, such as alumina or silica. Instead, the catalyst employed in this invention beneficially comprises a rare earth halide or rare earth oxyhalide that uniquely functions both as a catalyst support and as a source of a further catalytically active rare earth component. Unlike many heterogeneous catalysts of the prior art, the rare earth halide catalyst of this invention is beneficially soluble in water. Accordingly, should process equipment, such as filters, valves, circulating tubes, and small or intricate parts of reactors, become plugged with particles of the rare earth halide catalyst, then a simple water wash can advantageously dissolve the plugged particles and restore the equipment to working order. As a further advantage, the rare earth halide and rare earth oxyhalide catalysts employed in the process of this invention exhibit acceptable reaction rates and evidence of long lifetimes. Essentially no deactivation of these catalysts has been observed over the run times tested.

All of the aforementioned properties render the process of this invention uniquely attractive for converting methane and halogenated C_1 hydrocarbons into more highly halogenated C_1 hydrocarbons, which have utility in a variety of commercially significant syntheses. As a most preferred advantage, the process of this invention can be employed to monohalogenate methane selectively to methyl halides, including methyl chloride and methyl bromide, which are advantageously converted in downstream processes into valuable commodity chemicals, such as methyl alcohol, dimethyl ether, light olefins, gasolines, vinyl halide monomer, and acetic acid.

In a second aspect, this invention provides for a novel process of preparing methyl alcohol, dimethyl ether, or a combination thereof. The process in this aspect comprises (a)

contacting methane with a source of halogen and, optionally, a source of oxygen in the presence of a catalyst comprising a rare earth halide or rare earth oxyhalide under monohalogenation process conditions sufficient to prepare methyl halide, the rare earth halide or rare earth oxyhalide catalyst being substantially free of copper and iron, with the proviso that when cerium is present in the catalyst, then at least one other rare earth element is also present in the catalyst; and thereafter (b) contacting the methyl halide thus produced with water under hydrolysis conditions sufficient to prepare methyl alcohol, dimethyl ether, or a combination thereof and co-product hydrogen halide; and optionally (c) recycling the co-product hydrogen halide to the oxidative halogenation process of step (a).

In this second aspect of the invention, methane is beneficially converted into methyl alcohol via intermediate methyl halide. The method of this invention advantageously produces methyl alcohol without the use of synthesis gas. Accordingly, a syngas reactor, which involves costly steam reforming or partial oxidation units, is not needed for the process of this invention. Instead, the engineering employed in the process of this invention is conventional and cost effective. Accordingly, the process invention can be readily accommodated in remote locations around the world where methane sources are currently stranded. Since methyl alcohol is more easily and safely transported than methane gas, the conversion of methane to methyl alcohol by the simple process of this invention would free inaccessible methane resources.

In a third aspect, this invention provides for a novel process of preparing light olefins and/or gasolines. In this aspect, the process comprises (a) contacting methane with a source of halogen and, optionally, a source of oxygen in the presence of a catalyst comprising a rare earth halide or rare earth oxyhalide compound under oxidative halogenation process conditions sufficient to prepare methyl halide and, optionally, dihalomethane, the rare earth halide or rare earth oxyhalide catalyst being substantially free of copper and iron, and with the proviso that when cerium is present in the catalyst, at least one other rare earth element is also present in the catalyst; and thereafter (b) contacting the methyl halide and, optionally, dihalomethane thus produced with a condensation catalyst under condensation conditions sufficient to prepare at least one light olefin, a higher hydrocarbon, or a combination thereof, and co-product hydrogen halide; and optionally, (c) recycling the co-product hydrogen halide to the oxidative halogenation process of step (a). For the purposes of this third aspect of the invention, a "light olefin" shall be identified as

ethylene, propylene, butenes, or a mixture thereof, and a "higher hydrocarbon" shall be identified as a C5+ hydrocarbon.

In this third aspect of the invention, methane is activated via intermediate methyl halide to form light olefins, such as ethylene, propylene, and/or butenes, and/or higher hydrocarbons, such as C5+ gasolines. In the production of light olefins, the novel process of this invention eliminates the need for costly, energy intensive, and complex steam cracker technology. Instead, highly valuable commodity olefins are produced with substantially simpler engineering while beneficially utilizing methane resources that are currently under-utilized or wasted. Likewise, the aforementioned novel process converts methane via intermediate methyl halide to C5+ gasolines. Thus, complicated hydrocarbon conversion processes that are associated with petroleum refineries and Fischer-Tropsch facilities are eliminated with the instant simple invention.

In a fourth aspect, this invention provides for a novel process of preparing vinyl halide monomer. In this aspect, the process comprises (a) contacting methane with a first source of halogen and, optionally, a first source of oxygen in the presence of a first oxidative halogenation catalyst under oxidative halogenation process conditions sufficient to prepare methyl halide and, optionally, dihalomethane, the catalyst comprising a rare earth halide or rare earth oxyhalide, being substantially free of copper and iron, with the proviso that when cerium is present in the catalyst, then at least one other rare earth element is also present in the catalyst; (b) contacting the methyl halide and, optionally, dihalomethane thus produced with a condensation catalyst under condensation conditions sufficient to prepare ethylene and co-product hydrogen halide; (c) contacting the ethylene with a second source of halogen and, optionally, a second source of oxygen, in the presence of a second oxidative halogenation catalyst under oxidative halogenation process conditions sufficient to prepare vinyl halide monomer; and optionally (d) recycling the co-product hydrogen halide from step (b) to steps (a) and/or (c). Conversion of ethylene to vinyl halide monomer in step (c) can be effected by conventional prior art catalysts, for example, supported copper catalysts, that produce 1,2-dihaloethane, which subsequently is thermally cracked to vinyl halide monomer typically in a separate thermal cracker. Alternatively, conversion of ethylene to vinyl halide monomer in step (c) can be effected by use of the aforementioned catalyst comprising a rare earth halide or rare earth oxyhalide compound, essentially free of iron and copper, and with the proviso that when cerium is present in the catalyst, then at least one

other rare earth element is also present in the catalyst. When the rare earth catalyst is used, then vinyl halide is formed directly without the need for a separate thermal cracking reactor. Vinyl halide can also be made by mixing the ethylene produced in step (b) with a methane feed to step (a) to yield a reactor effluent from step (a) containing methyl halide and vinyl halide. In this design, the first and second sources of halogen, the first and second sources of oxygen, and the first and second oxidative halogenation catalysts are in each instance identical, since steps (a) and (c) are combined in the same reactor. Accordingly, separation of methyl halide and vinyl halide prior to conversion of the methyl halide to ethylene provides a two-reactor system of producing vinyl halide from methane.

In this fourth aspect, the invention involves a novel integrated process for activating methane to form methyl halide, then condensing methyl halide to ethylene and co-product hydrogen halide, and thereafter, directly utilizing the stream containing ethylene and hydrogen halide in an oxidative halogenation process of converting ethylene to vinyl halide monomer. In a preferred method of conducting this process as described hereinabove, the step to produce methyl halide and the step to produce vinyl halide monomer are combined in one reactor. Accordingly, the process can be beneficially convert methane to vinyl halide monomer in a two-reactor system.

In a fifth aspect, this invention provides for a novel integrated process of preparing acetic acid. In this aspect the process comprises (a) contacting methane with a source of halogen and, optionally, a source of oxygen in the presence of an oxidative halogenation catalyst under oxidative halogenation process conditions sufficient to prepare methyl halide; (b) contacting the methyl halide thus produced with a carbonylation agent in the presence of a carbonylation catalyst under carbonylation conditions sufficient to prepare acetyl halide; and thereafter (c) hydrolyzing the acetyl halide under hydrolysis conditions to produce acetic acid. In a preferred embodiment of this invention, the oxidative halogenation catalyst comprises a rare earth halide or rare earth oxyhalide, being substantially free of copper and iron, with the proviso that when cerium is present in the catalyst, then at least one other rare earth element is also present in the catalyst

In this fifth aspect of the invention, a novel synthesis is provided for the production of acetic acid. This unique synthesis is characterized by its use of methane as a raw material, the use of methyl halide as an intermediate in the production of acetic acid, and the absence of methanol as an intermediate in the process.

In the novel oxidative halogenation process of this invention, a halogenated C_1 hydrocarbon product, preferably a monohalogenated C_1 hydrocarbon product, is selectively produced with essentially no formation of perhalogenated C_1 chlorocarbon product and with advantageously low levels of by-products, such as, CO_x oxygenates (CO and CO_2). The novel process of this invention comprises contacting a reactant hydrocarbon selected from methane, a halogenated C_1 hydrocarbon, or a mixture thereof, with a source of halogen and, optionally, a source of oxygen in the presence of a catalyst under process conditions sufficient to prepare a halogenated C_1 hydrocarbon having a greater number of halogen substituents as compared with the reactant hydrocarbon. The use of a source of oxygen is preferred. The unique catalyst employed in the oxidative halogenation process of this invention comprises a rare earth halide or rare earth oxyhalide compound that is substantially free of copper and iron, with the further proviso that when cerium is present in the catalyst, at least one other rare earth element is also present in the catalyst.

In the process of this invention, the source of halogen may be provided, for example, as elemental halogen or hydrogen halide. If the source is elemental halogen, then the halogen itself functions in a dual role to provide a halogen ion and an oxidation agent for the oxidative halogenation process. In this instance, the reaction products will include a halogen acid. Advantageously, the halogen acid can be recycled and used with a source of oxygen in the feed to effect the process of this invention. Accordingly, there is no need to regenerate elemental halogen from the product halogen acid.

In a preferred embodiment, the process of this invention provides for the oxidative halogenation of methane to form methyl halide and, optionally dihalomethane. In this preferred embodiment, the process comprises contacting methane with a source of halogen and, optionally, a source of oxygen in the presence of the aforementioned rare earth halide or rare earth oxyhalide catalyst under process conditions sufficient to prepare methyl halide and, optionally, dihalomethane, the rare earth halide or rare earth oxyhalide catalyst being substantially free of copper and iron, and with the further proviso that when cerium is present in the catalyst, at least one other rare earth element is also present in the catalyst.

In a more preferred embodiment, the process of this invention provides for the oxidative monochlorination of methane to form methyl chloride in high selectivity. In this more preferred embodiment, the process comprises contacting methane with a source of chlorine, most preferably, hydrogen chloride, and a source of oxygen in the presence of a

catalyst comprising lanthanum chloride or lanthanum oxychloride under process conditions sufficient to prepare methyl chloride, the lanthanum chloride or lanthanum oxychloride catalyst being substantially free of copper and iron.

In a more preferred embodiment of this invention, the rare earth halide or rare earth oxyhalide catalyst is "porous," which, for the purposes of this invention, means that the catalyst has a surface area of least 3 m^2/g, as determined by the BET (Brunauer-Emmet-Teller) method of measuring surface area, described by S. Brunauer, P. H. Emmett, and E. Teller, *Journal of the American Chemical Society*, 60, 309 (1938). In another more preferred embodiment of this invention, the rare earth halide is lanthanum chloride, and the rare earth oxyhalide is lanthanum oxychloride.

The novel oxidative halogenation process, described hereinabove, may be beneficially integrated with downstream processes to convert methyl halides into highly valuable commodity chemicals, including methyl alcohol, dimethyl ether, light olefins, such as ethylene, propylene, and butenes, and higher hydrocarbons, including C5+ gasolines, as well as vinyl halide monomer and acetic acid.

Accordingly, in a second aspect, this invention provides for a novel process of preparing methyl alcohol, dimethyl ether, or a combination thereof. The process in this aspect comprises (a) contacting methane with a source of halogen and, optionally, a source of oxygen in the presence of a catalyst comprising a rare earth halide or rare earth oxyhalide under monohalogenation process conditions sufficient to prepare methyl halide, the rare earth halide or rare earth oxyhalide catalyst being substantially free of copper and iron, with the proviso that when cerium is present in the catalyst, then at least one other rare earth element is also present in the catalyst; and thereafter (b) contacting the methyl halide thus produced with water under hydrolysis conditions sufficient to prepare methyl alcohol, dimethyl ether, or a combination thereof and co-product hydrogen halide; and optionally (c) recycling the co-product hydrogen halide to the oxidative halogenation process of step (a).

In a third aspect, this invention provides for a novel process of preparing light olefins and/or gasolines, the process comprising (a) contacting methane with a source of halogen and, optionally, a source of oxygen in the presence of a catalyst comprising a rare earth halide or rare earth oxyhalide compound under oxidative halogenation process conditions sufficient to prepare methyl halide and, optionally, dihalomethane, the rare earth halide or rare earth oxyhalide catalyst being substantially free of copper and iron, and with

the proviso that when cerium is present in the catalyst, at least one other rare earth element is also present in the catalyst; and thereafter (b) contacting the methyl halide and, optionally, dihalomethane thus produced with a condensation catalyst under condensation conditions sufficient to prepare at least one light olefin, a higher hydrocarbon, or a combination thereof, and co-product hydrogen halide; and optionally, (c) recycling the co-product hydrogen halide to the oxidative halogenation process of step (a). For the purposes of this third aspect of the invention, a "light olefin" shall be identified as ethylene, propylene, butenes, or a mixture thereof, and a "higher hydrocarbon" shall be identified as a C5+ hydrocarbon.

In a fourth aspect, this invention provides for a novel process of preparing vinyl halide monomer, the process comprising (a) contacting methane with a first source of halogen and, optionally, a first source of oxygen in the presence of a first oxidative halogenation catalyst under oxidative halogenation process conditions sufficient to prepare methyl halide and, optionally, dihalomethane, the catalyst comprising a rare earth halide or rare earth oxyhalide, being substantially free of copper and iron, with the proviso that when cerium is present in the catalyst, then at least one other rare earth element is also present in the catalyst; (b) contacting the methyl halide and, optionally, dihalomethane thus produced with a condensation catalyst under condensation conditions sufficient to prepare ethylene and co-product hydrogen halide; (c) contacting the ethylene with a second source of halogen and, optionally, a second source of oxygen, in the presence of a second oxidative halogenation catalyst under oxidative halogenation process conditions, and optional thermal cracking conditions, sufficient to prepare vinyl halide monomer; and optionally (d) recycling the co-product hydrogen halide from step (b) to steps (a) and (c).

Advantageously, the conversion of ethylene to vinyl halide monomer in step (c) hereinabove can be effected by conventional prior art catalysts, such as copper halides, or by use of the rare earth halide or rare earth oxyhalide compound, described previously. Vinyl halide can also be made by mixing the ethylene produced in step (b) with the methane feed to step (a) to yield a reactor effluent from step (a) containing methyl halide and vinyl halide.

In a fifth aspect, this invention provides for a novel integrated process of preparing acetic acid. In this aspect the process comprises (a) contacting methane with a source of halogen and, optionally, a source of oxygen in the presence of an oxidative halogenation catalyst under oxidative halogenation process conditions sufficient to prepare methyl halide; (b) contacting the methyl halide thus produced with a carbonylation agent in the presence of

a carbonylation catalyst under carbonylation conditions sufficient to prepared acetyl halide; and thereafter (c) hydrolyzing the acetyl halide under hydrolysis conditions to produce acetic acid. In a preferred embodiment of this invention, the oxidative halogenation catalyst comprises a rare earth halide or rare earth oxyhalide, being substantially free of copper and iron, with the proviso that when cerium is present in the catalyst, then at least one other rare earth element is also present in the catalyst.

Each of above-identified downstream applications will be described in detail following a full description herein of the novel oxidative halogenation process.

The reactant hydrocarbon used in the oxidative halogenation process of this invention comprises methane or any halogenated C_1 hydrocarbon that is capable of acquiring halogen substituents in accordance with the process described herein. The halogen substituent of the halogenated C_1 hydrocarbon is preferably selected from the group consisting of chlorine, bromine, and iodine, more preferably, chlorine and bromine. One, two, or three halogen substituents may be present on the halogenated C_1 hydrocarbon; but for the purposes of the reactant hydrocarbon, the C_1 reactant is not a perhalogenated compound, as in carbon tetrachloride. Different halogen substituents may be suitably present in the C_1 hydrocarbon reactant, as illustrated by bromodichloromethane and dibromodichloromethane.

Suitable examples of halogenated C_1 hydrocarbons include, without limitation, methyl chloride, methyl bromide, methyl iodide, dichloromethane, dibromomethane, diiodomethane, chloroform, tribromomethane, bromodichloromethane, iododichloromethane, chlorodibromomethane, iododibromomethane, and the like. Methane, however, is the most preferred reactant hydrocarbon. The C_1 reactant hydrocarbon may be provided to the oxidative halogenation process as a pure feed stream, or diluted with an inert diluent as described hereinafter, or as a mixture of methane and halogenated C_1 hydrocarbon, optionally, further in combination with an inert diluent.

The source of halogen, which is employed in the process of this invention, may be any inorganic or organic halogen-containing compound (or mixture of such compounds) that is capable of transferring its halogen atom(s) to the reactant hydrocarbon. Suitable non-limiting examples of the source of halogen include chlorine, bromine, iodine, hydrogen chloride, hydrogen bromide, hydrogen iodide, and halogenated hydrocarbons having one or more labile halogen substituents (i.e., transferable halogen substituents), the latter preferably

being perhalocarbons or highly halogenated hydrocarbons having two or more halogen atoms. Non-limiting examples of perhalocarbons with labile halogen substituents include carbon tetrachloride, carbon tetrabromide, and the like. Non-limiting examples of highly halogenated hydrocarbons having two or more halogen substituents, at least one substituent of which is labile, include chloroform and tribromomethane. Preferably, the source of halogen is a source of chlorine or a source of bromine, more preferably, hydrogen chloride or hydrogen bromide, most preferably, hydrogen chloride.

The source of halogen may be provided to the process in any amount that is effective in producing the desired halogenated C_1 hydrocarbon product. Typically, the amount of halogen source will vary depending upon the specific process stoichiometry, the reactor design, and safety considerations. It is possible, for example, to use a stoichiometric amount of halogen source with respect to the reactant hydrocarbon or with respect to oxygen, if oxygen is present. Alternatively, the source of halogen may be used in an amount that is greater or less than the stoichiometric amount, if desired. In one embodiment illustrative of the invention, methane can be oxidatively chlorinated with chlorine to form methyl chloride and hydrogen chloride, the stoichiometric reaction of which is shown hereinbelow in Equation III:

$$CH_4 + Cl_2 \text{ ----> } CH_3Cl + HCl \qquad \text{(III)}$$

The aforementioned process, which does not employ oxygen, is typically conducted "fuel-rich," that is, with an excess of hydrocarbon reactant; but the process conditions are not limited to fuel-rich modes of operation. Other operating conditions outside the fuel-rich limits may also be suitable. Typically, the molar ratio of reactant hydrocarbon to source of halogen (expressed as molecular halogen, for example, Cl_2) is greater than 1/1, preferably, greater than 2/1, and more preferably, greater than 4/1. Generally, the molar ratio of reactant hydrocarbon to source of halogen is less than 20/1, preferably, less than 15/1, and more preferably, less than 10/1.

In a preferred embodiment illustrative of the invention, methane can be oxidatively chlorinated with hydrogen chloride in the presence of oxygen to produce methyl chloride and water, the stoichiometric reaction of which is shown hereinafter in Equation IV:

$$CH_4 + HCl + \tfrac{1}{2} O_2 \text{ ----> } CH_3Cl + H_2O \qquad \text{(IV)}$$

This type of reaction, which employs oxygen, is usually conducted "fuel-rich," due to safety considerations. With respect to this embodiment, the term "fuel-rich" means that oxygen is the limiting reagent and a molar excess of C_1 reactant hydrocarbon is used relative to oxygen. Typically, for example, the molar ratio of hydrocarbon to oxygen is chosen for operation outside the fuel-rich flammability limit of the mixture, although this is not absolutely required. In addition, a stoichiometric (for example, 1 HCl:0.5 O_2) or greater than stoichiometric molar ratio of hydrogen halide to oxygen is typically employed to maximize the yield of halogenated hydrocarbon product.

A source of oxygen is not required for the process of this invention; however, it is preferred to use a source of oxygen, particularly when the source of halogen contains hydrogen atoms. The source of oxygen can be any oxygen-containing gas or mixture of such gases, such as, essentially pure molecular oxygen, air, oxygen-enriched air, or a mixture of oxygen with a diluent gas that does not interfere with the oxidative halogenation process, such as, nitrogen, argon, helium, carbon monoxide, carbon dioxide, methane, and mixtures thereof. As noted above, when oxygen is employed, the feed to the oxidative halogenation reactor is generally fuel-rich. Typically, the molar ratio of reactant hydrocarbon to oxygen is greater than 2/1, preferably, greater than 4/1, and more preferably, greater than 5/1. Typically, the molar ratio of reactant hydrocarbon to oxygen is less than 20/1, preferably, less than 15/1, and more preferably, less than 10/1.

Based on the description hereinabove, one skilled in the art will know how to determine the molar quantities of reactant hydrocarbon, source of halogen, and source of oxygen suitable for reactant combinations that may be different from those illustrated hereinabove.

Optionally, if desired, the feed, comprising reactant hydrocarbon, source of halogen, and preferably, source of oxygen, can be diluted with a diluent or carrier gas, which may be any essentially non-reactive gas, that is, a gas that does not substantially interfere with the oxidative halogenation process. The diluent may assist in removing products and heat from the reactor and in reducing the number of undesirable side-reactions. Non-limiting examples of suitable diluents include nitrogen, argon, helium, carbon monoxide, carbon dioxide, and mixtures thereof. In an alternative embodiment, methane may be used as a diluent, although methane is reactive in this process. The quantity of diluent employed is typically greater than 10 mole percent, and preferably, greater than 20 mole percent, based

on the total moles of feed to the reactor, that is, total moles of reactant hydrocarbon, source of halogen, source of oxygen, and diluent. The quantity of diluent employed is typically less than 90 mole percent, and preferably, less than 70 mole percent, based on the total moles of feed to the reactor.

The catalyst employed in the oxidative halogenation process of this invention comprises, in one aspect, a rare earth halide compound. The rare earths are a group of 17 elements consisting of scandium (atomic number 21), yttrium (atomic number 39) and the lanthanides (atomic numbers 57-71) [James B. Hedrick, U.S. Geological Survey - Minerals Information - 1997, "Rare-Earth Metals"]. Preferably, herein, the term is taken to mean an element selected from lanthanum, cerium, neodymium, praseodymium, dysprosium, samarium, yttrium, gadolinium, erbium, ytterbium, holmium, terbium, europium, thulium, lutetium, and mixtures thereof. Preferred rare earth elements for use in the aforementioned oxidative halogenation process are those that are typically considered as being single valency metals. The catalytic performance of rare earth halides using multi-valency metals appears to be less desirable than rare earth halides using single valency metals. The rare earth element for this invention is preferably selected from the group consisting of lanthanum, neodymium, praseodymium, dysprosium, yttrium, and mixtures thereof. Most preferably, the rare earth element used in the catalyst is lanthanum or a mixture of lanthanum with other rare earth elements.

Preferably, the rare earth halide is represented by the formula MX_3 wherein M is at least one rare earth element selected from the group consisting of lanthanum, cerium, neodymium, praseodymium, dysprosium, samarium, yttrium, gadolinium, erbium, ytterbium, holmium, terbium, europium, thulium, lutetium, and mixtures thereof; and wherein X is selected from the group consisting of chloride, bromide, iodide, and mixtures thereof. More preferably, X is chloride, and the more preferred rare earth halide is represented by the formula MCl_3, wherein M is defined hereinbefore. Most preferably, X is chloride, and M is lanthanum or a mixture of lanthanum with other rare earth elements.

In a preferred embodiment, the rare earth halide is porous, meaning that typically the rare earth halide has a BET surface area of greater than 3 m^2/g, preferably, greater than 5 m^2/g. More preferably, the BET surface area is greater than 10 m^2/g, even more preferably, greater than 15 m^2/g, as an even higher preference, greater than 20 m^2/g, and most preferably, greater than 30 m^2/g. Generally, the BET surface area of the rare earth halide is

less than 200 m^2/g. For these above measurements, a nitrogen adsorption isotherm was measured at 77K and the surface area was calculated from the isotherm data utilizing the BET method, as referenced earlier herein.

In another aspect, the catalyst employed in this invention comprises a rare earth oxyhalide, the rare earths being the seventeen elements identified hereinabove. Preferably, the rare earth oxyhalide is represented by the formula MOX, wherein M is at least one rare earth element selected from the group consisting of lanthanum, cerium, neodymium, praseodymium, dysprosium, samarium, yttrium, gadolinium, erbium, ytterbium, holmium, terbium, europium, thulium, lutetium, and mixtures thereof; and wherein X is selected from the group consisting of chloride, bromide, iodide, and mixtures thereof. More preferably, the rare earth halide is a rare earth oxychloride, represented by the formula MOCl, wherein M is defined hereinbefore. Most preferably, M is lanthanum or lanthanum with a mixture of other rare earth elements.

In a preferred embodiment, the rare earth oxyhalide is also porous, which for the oxyhalide generally implies a BET surface area of greater than 12 m^2/g. Preferably, the rare earth oxyhalide has a BET surface area of greater than 15 m^2/g, more preferably, greater than 20 m^2/g, and most preferably, greater than 30 m^2/g. Generally, the BET surface area of the rare earth oxyhalide is less than 200 m^2/g. In addition, it is noted that the MOCl phases possess characteristic powder X-Ray Diffraction (XRD) patterns that are distinct from the MCl_3 phases.

In general, the presence in the catalyst of metals that are capable of oxidation-reduction (redox) is undesirable. Redox metals typically include transition metals that have more than one stable oxidation state, such as iron, copper, and manganese. The rare earth halide or oxyhalide catalyst of this invention is specifically required to be substantially free of copper and iron. The term "substantially free" means that the atom ratio of rare earth element to redox metal, preferably iron or copper, is greater than 1/1, preferably greater than 10/1, more preferably greater than 15/1, and most preferably greater than 50/1. In addition, cerium, a lanthanide rare earth element, is known to be an oxidation-reduction catalyst having the ability to access both the 3^+ and 4^+ oxidation states. For this reason, if the rare earth metal is cerium, the catalyst of this invention further comprises at least one more rare earth metal other than cerium. Preferably, if one of the rare earth metals is cerium, the cerium is provided in a molar ratio that is less than the total amount of other rare earth

metals present in the catalyst. More preferably, however, substantially no cerium is present in the catalyst. By "substantially no cerium" it is meant that any cerium present is in an amount less than 10 atom percent, preferably, less than 5 atom percent, and even more preferably, less than 1 atom percent of the total rare earth components.

In an alternative embodiment of this invention, the rare earth halide or rare earth oxyhalide catalyst, described hereinbefore, may be bound to, extruded with, or deposited onto a catalyst support, such as alumina, silica, silica-alumina, porous aluminosilicate (zeolite), silica-magnesia, bauxite, magnesia, silicon carbide, titanium oxide, zirconium oxide, zirconium silicate, or any combination thereof. In this embodiment, the conventional support is used in a quantity greater than 1 weight percent, but less than 90 weight percent, preferably, less than 70 weight percent, more preferably, less than 50 weight percent, based on the total weight of the catalyst and catalyst support.

It may also be advantageous to include other elements within the catalyst. For example, preferable elemental additives include alkali and alkaline earths, boron, phosphorous, sulfur, germanium, titanium, zirconium, hafnium, and combinations thereof. These elements can be present to alter the catalytic performance of the composition or to improve the mechanical properties (for example attrition-resistance) of the material. In a preferred embodiment, the elemental additive is calcium. In another preferred embodiment, the elemental additive is not aluminum or silicon. The total concentration of elemental additives in the catalyst is typically greater than 0.01 weight percent and typically less than 20 weight percent, based on the total weight of the catalyst.

The rare earth halide and rare earth oxyhalide compounds may be obtained commercially or prepared by methods published in the art. A method currently felt to be preferable for forming the porous rare earth oxyhalide (MOX) comprises the following steps: (a) preparing a solution of a halide salt of the rare earth element or elements in a solvent comprising either water, an alcohol, or mixtures thereof; (b) adding a base to cause the formation of a precipitate; and (c) collecting and calcining the precipitate in order to form the MOX. Preferably, the halide salt is a rare earth chloride salt, for example, any commercially available rare earth chloride. Typically, the base is a nitrogen-containing base selected from ammonium hydroxide, alkyl amines, aryl amines, arylalkyl amines, alkyl ammonium hydroxides, aryl ammonium hydroxides, arylalkyl ammonium hydroxides, and mixtures thereof. The nitrogen-containing base may also be provided as a mixture of a

nitrogen-containing base with other bases that do not contain nitrogen. Preferably, the nitrogen-containing base is ammonium hydroxide or tetra(alkyl)ammonium hydroxide, more preferably, tetra(C_{1-20} alkyl)ammonium hydroxide. Porous rare earth oxychlorides may also be produced by appropriate use of alkali or alkaline earth hydroxides, particularly, with the buffering of a nitrogen-containing base, although caution should be exercised to avoid producing substantially the rare earth hydroxide or oxide. The solvent in Step (a) is preferably water. Generally, the precipitation is conducted at a temperature greater than 0°C. Generally, the precipitation is conducted at a temperature less than 200°C, preferably, less than 100°C. The precipitation is conducted generally at ambient atmospheric pressure, although higher pressures may be used, as necessary, to maintain liquid phase at the precipitation temperature employed. The calcination is typically conducted at a temperature greater than 200°C, preferably, greater than 300°C, and less than 800°C, preferably, less than 600°C. Production of mixed carboxylic acid and rare earth chloride salts also can yield rare earth oxychlorides upon appropriate decomposition.

A method currently felt to be preferable for forming the porous rare earth halide (MX_3) catalyst comprises the following steps: (a) preparing a solution of a halide salt of the rare earth element or elements in a solvent comprising either water, an alcohol, or mixtures thereof; (b) adding a base to cause the formation of a precipitate; (c) collecting, washing and calcining the precipitate; and (d) contacting the calcined precipitate with a halogen source. Preferably, the rare earth halide is a rare earth chloride salt, such as any commercially available rare earth chloride. The solvent and base may be any of those mentioned hereinbefore in connection with the formation of MOX. Preferably, the solvent is water, and the base is a nitrogen-containing base, as previously described. The precipitation is generally conducted at a temperature greater than 0°C and less than 200°C, preferably less than 100°C, at ambient atmospheric pressure or a higher pressure so as to maintain liquid phase. The calcination is typically conducted at a temperature greater than 200°C, preferably, greater than 300°C, but less than 800°C, and preferably, less than 600°C. Preferably, the halogen source is a hydrogen halide, such as hydrogen chloride, hydrogen bromide, or hydrogen iodide. More preferably, the halogen source is hydrogen chloride. The contacting with the halogen source is typically conducted at a temperature greater than 100°C and less than 500°C. Typical pressures for the contacting with the source of halogen range from ambient atmospheric pressure to pressures less than 150 psia (1,034 kPa).

As noted hereinabove, the rare earth oxyhalide (MOX) compound can be converted into the rare earth halide (MX_3) compound by treating the oxyhalide with a source of halogen. Since the oxidative halogenation process of this invention requires a source of halogen, it is possible to contact the rare earth oxyhalide with a source of halogen, such as chlorine, in the oxidative halogenation reactor to form the MX_3 catalyst *in situ*.

The oxidative halogenation process of this invention can be conducted in a reactor of any conventional design suitable for gas phase processes, including batch, fixed bed, fluidized bed, transport bed, continuous and intermittent flow reactors, and catalytic distillation reactors. The process conditions (for example, molar ratio of feed components, temperature, pressure, gas hourly space velocity), can be varied widely, provided that the desired halogenated C_1 hydrocarbon product, preferably monohalogenated C_1 hydrocarbon product, more preferably, methyl chloride, is obtained. Typically, the process temperature is greater than 200°C, preferably, greater than 300°C, and more preferably, greater than 350°C. Typically, the process temperature is less than 600°C, preferably, less than 500°C, and more preferably, less than 450°C. Ordinarily, the process can be conducted at atmospheric pressure; but operation at higher or lower pressures is possible, as desired. Preferably, the pressure is equal to or greater than 14 psia (97 kPa), but less than 150 psia (1,034 kPa). Typically, the total weight hourly space velocity (WHSV) of the feed (reactant hydrocarbon, source of halogen, optional source of oxygen, and optional diluent) will be greater than 0.1 gram total feed per g catalyst per hour (h^{-1}), and preferably, greater than 0.5 h^{-1}. Typically, the total gas hourly space velocity of the feed will be less than 100 h^{-1}, and preferably, less than 20 h^{-1}.

If the oxidative halogenation process is conducted as described hereinabove, then a halogenated C_1 hydrocarbon product is formed that has a greater number of halogen substituents as compared with the reactant hydrocarbon. Halogenated C_1 hydrocarbon products beneficially produced by the oxidative halogenation process of this invention include, without limitation, methyl chloride, dichloromethane, methyl bromide, dibromomethane, methyl iodide, chloroform, and tribromomethane. Preferably, the halogenated C_1 hydrocarbon product is a monohalogenated C_1 hydrocarbon, a dihalogenated C_1 hydrocarbon, or a combination thereof. More preferably, the halogenated C_1 hydrocarbon product is a monohalogenated C_1 hydrocarbon. Even more preferably, the

halogenated C_1 hydrocarbon product is methyl chloride or methyl bromide; most preferably, methyl chloride.

For the purposes of the description herein, "conversion" shall be defined as the mole percentage of reagent compound that is converted, that is, reacted, in the oxidative halogenation process of this invention into product(s). Reference may be made to "conversion of reactant hydrocarbon," or "conversion of source of halogen," or "oxygen conversion." Conversions will vary depending upon the specific reactant being considered, specific catalyst, and specific process conditions. Typically, for the process of this invention, the conversion of methane or other reactant hydrocarbon is greater than 3 mole percent, and preferably, greater than 10 mole percent. Typically, for the process of this invention, the conversion of the source of halogen is greater than 12 mole percent, and preferably, greater than 20 mole percent. Typically, the oxygen conversion is greater than 10 mole percent, and preferably, greater than 20 mole percent.

For the purposes of this invention, "selectivity" shall be defined as the mole percentage of converted methane or other reactant C_1 hydrocarbon that is converted into a specific product, such as a halogenated C_1 hydrocarbon product or oxygenated by-product, such as CO or CO_2. In the oxidative halogenation process of this invention, the selectivity to monohalogenated C_1 hydrocarbon product, most preferably, methyl chloride or methyl bromide, is typically greater than 60 mole percent, preferably, greater than 70 mole percent, and more preferably, greater than 80 mole percent. The selectivity to dihalogenated C_1 hydrocarbon product, preferably dichloromethane or dibromomethane, is typically less than 20 mole percent, and preferably, less than 15 mole percent. Advantageously, the oxidative halogenation process of this invention produces essentially no perhalogenated product, such as, carbon tetrachloride and carbon tetrabromide, which have lower commercial value. By "essentially no perhalogenated product", it is intended that not more than five percent of perhalogenated species should be produced in the process and in combination with the desired halogenated C_1 hydrocarbon product, but preferably not more than two percent, and most preferably not more than one percent of perhalogenated species should be produced. As a further advantage, in preferred embodiments of this invention low levels of oxygenated by-products, such as CO_x oxygenates (CO and CO_2) are produced. Typically, the total selectivity to carbon monoxide and carbon dioxide is less than 20 mole percent, preferably, less than 15 mole percent, and more preferably, less than 10 mole percent.

The monohalogenated and dihalogenated hydrocarbon products, preferably, monohalogenated products, more preferably, methyl chloride or methyl bromide, which are produced in the oxidative halogenation process of this invention, can be utilized as a feed in downstream processes that produce high-value commodity chemicals, such as methyl alcohol, dimethyl ether, light olefins, including ethylene, propylene, and butenes; higher hydrocarbons, including C5+ gasolines; vinyl halide monomer, and acetic acid. The hydrolysis of methyl halides to form methyl alcohol has been previously described in the art, representative citations of which include US 1,086,381, US 4,990,696, US 4,523,040, US 5,969,195, and as disclosed by G. Olah in *Journal of the American Chemical Society*, **1985**, 107, 7097-7105, and I. Fells, *Fuel Society Journal*, **10**, 1959, 26-35. For the example of methyl chloride hydrolysis to methyl alcohol, the process can be represented by the following stoichiometric reaction (V):

$$CH_3Cl + H_2O \longrightarrow CH_3OH + HCl \qquad (V)$$

Any catalyst can be employed for the hydrolysis of methyl halides, provided that the hydrolysis produces methyl alcohol. Many catalysts exhibit activity for this hydrolysis including, for example, alumina; various zeolites of the ZSM structure code, such as ZSM-5, preferably, having a Constraint Index from 1 to 12; alkali and alkaline earth metal hydroxides and alkoxides, such as sodium hydroxide, potassium hydroxide, and sodium ethoxide; alkyl ammonium hydroxides and various amines, for example, trimethylamine hydroxide and piperidine; transition metal halide complexes, preferably, halide complexes of platinum, palladium, and nickel, and mixtures thereof, more preferably, the chloride complexes thereof, optionally including a cation of H^+, Group IA, or Group IIA elements, such as K^+ or Na^+; and metal oxide/hydroxide catalysts, including the metal oxides/hydroxides of Group IIA elements (for example, Mg, Ba); as well as the entire series of transition elements (for example, V, Cr, Zr, Ti, Fe, or Zn), supported on γ-alumina or activated carbon.

The hydrolysis process conditions can vary depending upon the particular catalyst and alkyl halide employed. Since the thermodynamics favor the reverse reaction to form methyl halide (that is, Equation V in reverse), an excess of water relative to methyl halide is typically employed to drive the equilibrium towards methyl alcohol. Preferably, the molar ratio of water to methyl halide is greater than 1:1, more preferably, greater than 5:1. Preferably, the water/methyl halide molar ratio is less than 20:1, more preferably, less than

10:1. Generally, the hydrolysis is conducted at a temperature greater than 85°C, and preferably, greater than 115°C. Generally, the hydrolysis is conducted at a temperature less than 600°C, and preferably, less than 400°C. The process pressure can also vary from subatmospheric to superatmospheric; but generally ranges from greater than 7 psia (50 kPa), and preferably, greater than 14 psia (97 kPa), to less than 725 psia (4,999 kPa), and preferably, less than 73 psia (500 kPa). The weight hourly space velocity (WHSV) of the methyl halide feed can vary widely from a value typically greater than 0.1 g feed per g catalyst per hour (h^{-1}) to a value less than 1,000 h^{-1}. Preferably, the weight hourly space velocity of the methyl halide feed ranges from greater than 1 h^{-1} to less than 10 h^{-1}.

The conversion of methyl halide, that is, the mole percentage of methyl halide reacted relative to methyl halide in the feed, will vary depending upon the specific catalyst and process conditions. Generally, methyl alcohol and dimethyl ether are the predominant products, in varying ratios depending upon the catalyst and process conditions. Further details of the hydrolysis process and product distribution can be found in the pertinent references cited hereinabove. Hydrogen halide, which is a co-product of the hydrolysis process, can be conveniently recycled to the oxidative halogenation reactor, where it can be consumed as a source of halogen.

In another aspect of this invention, the methyl halide prepared by the aforementioned oxidative halogenation of methane can be condensed to form light olefins, such as ethylene, propylene, butenes, and higher hydrocarbons, including C5+ gasolines. For the example of methyl chloride being converted into ethylene, the stoichiometric reaction can be represented by the following Equation (VI):

$$2\ CH_3Cl \longrightarrow CH_2{=}CH_2 + 2\ HCl \qquad \text{(VI)}$$

As seen from the above, hydrogen halide, such as hydrogen chloride, is produced as a co-product of this condensation process. Again, the hydrogen halide can be conveniently recycled to the oxidative halogenation reactor and consumed as a source of halogen.

Any catalyst capable of effecting the condensation process can be employed. US 5,397,560, for example, discloses the use of aluminosilicates having a DCM-2 structure code for the conversion of methyl halides into light olefins, predominantly ethylene and propylene. Catalysts known for the condensation of methyl alcohol to light olefins and gasolines can also be employed analogously for the condensation described herein of methyl halides into light olefins and gasolines. Non-limiting examples of such catalysts include

zeolites of the ZSM structure code, such as ZSM-5, ZSM-11, ZSM-12, ZSM-34, ZSM-35, and ZSM-38, preferably, wherein the aforementioned ZSM zeolite has a Constraint Index from 1 to 12; as well as various aluminophosphates (ALPO's) and silicoaluminophosphates (SAPO's). References disclosing one or more of the aforementioned catalysts include US 3,894,107, US 4,480,145, US 4,471,150, US 4,769,504, US 5,912,393.

Generally, the condensation process involves contacting methyl halide with the catalyst under condensation process conditions sufficient to prepare at least one light olefin, such as ethylene, propylene, butenes, or at least one C5+ hydrocarbon, or any mixture thereof. The process temperature typically is greater than 250°C, and preferably, greater than 350°C. The process temperature is typically less than 600°C, and preferably, less than 450°C. The process pressure can vary from subatmospheric to superatmospheric; but generally a pressure greater than 0.1 psi absolute (689 Pa) and less than 300 psi absolute (2,068 kPa) is employed. The weight hourly space velocity (WHSV) of the methyl halide feed can vary widely from a value typically greater than 0.1 g feed per g catalyst per hour (h^{-1}) to a value less than 1,000 h^{-1}. Preferably, the weight hourly space velocity of the methyl halide feed ranges from greater than 1 h^{-1} to less than 10 h^{-1}. The product distribution of the aforementioned condensation process will vary depending upon the specific feed, catalyst, and process conditions. A product stream comprising light olefins, predominantly ethylene, propylene, and butenes, is generally obtained with the DCM-2 catalyst. A product stream containing predominantly heavier hydrocarbons, such as C5+ gasolines, is generally obtained with zeolite ZSM catalysts. Again, the hydrogen halide, obtained as a co-product of the process, can be conveniently recycled to the oxidative halogenation reactor and consumed as a source of halogen.

In a further application of this invention, ethylene obtained from the condensation of methyl halide can be fed directly into a vinyl halide monomer process, wherein the ethylene is contacted with a source of halogen, preferably the hydrogen halide, and optionally, a source of oxygen in the presence of an oxidative halogenation catalyst. Preferably, a source of oxygen is used. For the purposes of making vinyl halide monomer, the source of halogen and the source of oxygen can be any of those sources of halogen and sources of oxygen described hereinbefore in connection with the oxidative halogenation of methane. For the purposes of preparing vinyl halide monomer, the oxidative halogenation catalyst can be any conventional catalyst known for such a purpose, including supported copper catalysts, such

as, supported copper chloride promoted with alkali or alkaline earth halides, known to those skilled in the art. When these conventional catalysts are used, then dihaloethane is obtained, which is subsequently thermally cracked to vinyl halide monomer. In a preferred embodiment, the oxidative halogenation catalyst is the rare earth halide or rare earth oxyhalide catalyst described hereinbefore in connection with the oxidative halogenation of methane. When the rare earth halide or oxyhalide is used, then vinyl halide is obtained directly without the need for a separate thermal cracking reactor. Vinyl halide can also be made by mixing ethylene with the methane feed to the methane oxidative halogenation reactor so as to obtain an effluent containing both methyl halide and vinyl halide. Separation of methyl halide and vinyl halide prior to conversion of the methyl halide to ethylene beneficially provides a two-reactor system of producing vinyl halide from methane.

Typically, in the preparation of vinyl halide the molar ratio of ethylene to oxygen is greater than 2/1, preferably, greater than 4/1, and generally, less than 20/1, and preferably, less than 15/1. Generally, the oxidative halogenation of ethylene is carried out at a temperature greater than 150°C, preferably, greater than 200°C, and more preferably, greater than 250°C. Typically, the oxidative halogenation of ethylene is carried out at a temperature less than 500°C, preferably, less than 425°C, and more preferably, less than 350°C. Ordinarily, the process will be conducted at atmospheric pressure or a higher pressure. Typically, then, the pressure will be equal to or greater than 14 psia (101 kPa), but less than 150 psia (1,034 kPa). Typically, the total gas hourly space velocity (GHSV) of the reactant feed (ethylene, source of halogen, source of oxygen, and any optional diluent) will vary from greater than 10 ml total feed per ml catalyst per hour (h^{-1}), preferably, greater than 100 h^{-1}, to less than 50,000 h^{-1}, and preferably, less than 10,000 h^{-1}. Further details on catalyst and process conditions suitable for the oxidative halogenation of ethylene-containing streams to vinyl halide monomer can be found in International Patent Application Serial No. PCT/US00/27272, filed October 3, 2000.

In yet another aspect of this invention, the methyl halide, produced in the oxidative halogenation of methane, can be carbonylated with a carbonylation agent in the presence of a carbonylation catalyst to form acetyl halide, which thereafter can be hydrolyzed to form acetic acid. In the carbonylation step, any carbonylation process conditions can be used, provided that the carbonylation yields the desired acetyl halide product. The carbonylation agent, itself, can be any compound that is capable of transferring carbonyl (CO) to the

methyl halide. Preferably, the carbonylation agent is carbon monoxide or an organometallic complex containing labile carbon monoxide, such as, transition metal salts and complexes, including Group VIII salts and complexes, such as the salts and complexes of palladium, iron, and cobalt, further including the carbonyl complexes of said transition metals. The molar ratio of carbonylation agent to methyl halide is typically at least 1:1, and preferably, greater than 1:1. More preferably, the molar ratio of carbonylation agent to methyl halide is greater than 2:1. Preferably, the molar ratio of carbonylation agent to methyl halide is less than 20:1, more preferably, less than 10:1. Generally, the carbonylation step is conducted at a temperature greater than 50°C and at a temperature less than 350°C. The pressure may range typically from atmospheric to higher pressures, generally from greater than 7 psia (50 kPa) to less than 725 psia (4,999 kPa). The total weight hourly space velocity (WHSV) of the carbonylation feed, including methyl halide and carbonylation agent, can vary widely from a value typically greater than 0.1 g feed per g catalyst per hour (h^{-1}) to a value less than 1,000 h^{-1}.

The product of the carbonylation process is acetyl halide, preferably, acetyl chloride. The subsequent hydrolysis of acetyl halide to acetic acid is simply effected by contacting acetyl halide with water under process conditions sufficient to form acetic acid. One skilled in the art will know the details of the hydrolysis of acetyl halide, as this step is a straight-forward hydrolysis of an acyl halide, which is well known and described, for example, in numerous organic chemistry textbooks.

The following examples are provided to further illustrate of the process of this invention; but the examples should not be construed as limiting the invention in any manner. In light of the disclosure herein, those of skill in the art will recognize alternative embodiments of the invention that fall within the scope of the claims.

Example 1

A catalyst composition comprising a porous lanthanum oxychloride was prepared as follows. Lanthanum chloride ($LaCl_3 \cdot 7\ H_2O$, 15 g) was dissolved in deionized water (100 ml) in a round-bottom flask. Ammonium hydroxide (6 M, 20 ml) was added to the lanthanum chloride solution with stirring. The mixture was centrifuged, and the excess liquid was decanted to yield a gel. In a separate container, calcium lactate (0.247 g, 0.0008 moles) was dissolved to form a saturated solution in deionized water. The calcium lactate solution was added with stirring to the lanthanum-containing gel. The gel was dried at 120°

C overnight. A dried solid was recovered, which was calcined under air in an open container at 550°C for 4 hours to yield a porous lanthanum oxychloride catalyst (6.84 g). X-ray diffraction (XRD) of the solid indicated the presence of a quasi-crystalline form of lanthanum oxychloride.

The catalyst prepared hereinabove was crushed to 20 x 40 US mesh (0.85 x 0.43 mm) and evaluated in the oxidative chlorination of methane as follows. A tubular, nickel alloy reactor, having a ratio of length to diameter of 28.6/1 {6 inches (15.24 cm) x 0.210 inches (0.533 cm)} was loaded with catalyst (2.02 g). The reactor was fed a mixture of methane, hydrogen chloride, and oxygen in the ratios shown in Table 1. The operating temperature was 400°C, and the operating pressure was atmospheric. The exit gases were analyzed by gas phase chromatography. Results are set forth in Table 1.

Table 1. Oxychlorination of Methane Over Lanthanum Catalyst to Methyl Chloride

Mole Ratio CH_4:HCl:O_2	WHSV h^{-1}	Conv CH_4 (mol%)	Conv HCl (mol %)	Conv O_2 (mol%)	Sel CH_3Cl (mol %)	Sel CH_2Cl_2 (mol %)	Sel CO (mol %)	Sel CO_2 (mol %)
2:1:0.86	8.41	5.0	12.2	14.7	72.8	12.1	13.5	1.6
2:1:0.86	4.17	13.3	29.2	30.0	62.6	18.0	16.1	2.2
2:1:0.43	4.30	12.4	-	42.3	71.0	16.3	10.8	1.3
2:1:0.43	8.43	6.1	-	23.3	83.5	10.2	6.4	0.0

1. Process Conditions: 400°C, atmospheric pressure

The results in Table 1 show that a lanthanum oxychloride catalyst prepared as described hereinabove can be advantageously employed in the oxidative chlorination of methane. Methyl chloride was found to be the predominant product. Dichloromethane was formed as a secondary product. The production of oxygenated C_1 products, specifically carbon monoxide and carbon dioxide, was advantageously low.

Example 2

This example illustrates an oxidative chlorination utilizing both methane and ethylene as hydrocarbon feeds. The catalyst was prepared by the following method. A solution of lanthanum chloride in water was prepared by dissolving one part of commercially available hydrated lanthanum chloride (Alfa Aesar) in 6.6 parts of deionized water. Rapid addition with stirring of 1.34 parts 6 M ammonium hydroxide in water caused the formation of a gel. The mixture was centrifuged, and the solution was decanted away from the gel and discarded. The collected gel was dried at 120°C overnight and then calcined at 550°C for 4 hours in air to yield an example of the catalyst. The XRD pattern matched that of LaOCl.

The catalyst was loaded into a nickel reactor with length/diameter ratio of 20/1. The reactor was brought to operating conditions of 452°C and near-ambient pressure. A feed containing methane/ethylene/hydrogen chloride/argon/oxygen in a molar ratio of 2.68:0.30:1.99:0.16:1:00 was contacted with the catalyst at a space-time of 7.6 seconds. Conversions of the reactants were as follows: ethylene, 46.4 percent; methane, 17.4 percent; hydrogen chloride, 36.4 percent; oxygen, 44.2 percent (calculated as mole percentages). Both methane and ethylene were consumed. Molar carbon selectivities were as follows: vinyl chloride, 24.7 percent; 1,2-dichloroethane, 6.1 percent; dichloroethylenes, 5.8 percent; methyl chloride 38.3 percent; methylene dichloride, 12.5 percent; carbon monoxide, 11.3 percent; and carbon dioxide, 1.2 percent. The example illustrates the feasibility of converting a combined feed of methane and ethylene to methyl chloride and vinyl chloride in one reactor. The methyl chloride product can be thereafter condensed to additional ethylene, which can be recycled to the oxidative halogenation reactor for conversion to additional vinyl chloride. With quantitative conversion of the chlorinated methanes to ethylene in a condensation reactor, these

results allow calculation of an assumed product distribution for an envisioned methane to vinyl chloride process. Such a calculation yields molar selectivities on methane as follows: vinyl chloride monomer, 50.3 percent; 1,2-dichloroethane, 12.5 percent; 1,2-dichloroethylenes, 11.8 percent; carbon monoxide, 22.9 percent; and carbon dioxide, 2.5 percent.

CLAIMS:

1. A process of oxidative halogenation comprising contacting a reactant hydrocarbon selected from methane, a halogenated C_1 hydrocarbon, or a mixture thereof with a source of halogen and, optionally, a source of oxygen in the presence of a catalyst under process conditions sufficient to prepare a halogenated C_1 hydrocarbon having a greater number of halogen substituents as compared with the reactant hydrocarbon, the catalyst comprising a rare earth halide or rare earth oxyhalide substantially free of iron and copper, with the proviso that when cerium is present in the catalyst, then at least one other rare earth element is also present in the catalyst.

2. The process of Claim 1 wherein the reactant hydrocarbon is selected from the group consisting of methane, chloromethane, bromomethane, iodomethane, dichloromethane, dibromomethane, diiodomethane, chlorobromomethane, and mixtures thereof.

3. The process of Claims 1 or 2 wherein the source of halogen is selected from the group consisting of elemental halogens, hydrogen halides, and halogenated hydrocarbons having one or more labile halogen substituents.

4. The process of any one of Claims 1 to 3 wherein the source of halogen is a source of chlorine or a source of bromine, or wherein the source of halogen is hydrogen chloride.

5. The process of any one of Claims 1 to 4 wherein the process is conducted at a molar ratio of reactant hydrocarbon to source of halogen of greater than 1/1 to less than 20/1.

6. The process of any one of Claims 1 to 5 wherein the process further comprises oxygen.

7. The process of Claim 6 wherein the source of halogen is provided essentially in a stoichiometric or greater than stoichiometric amount with respect to the source of oxygen.

8. The process of Claim 6 or 7 wherein the source of oxygen is selected from the group consisting of molecular oxygen and air.

9. The process of any one of Claims 6 to 8wherein the process is conducted at a molar ratio of hydrocarbon to oxygen of greater than 2/1 and less than 20/1.

10. The process of any one of Claims 1 to 9 wherein the process further comprises a diluent selected from the group consisting of nitrogen, helium, argon, carbon monoxide, carbon dioxide, and mixtures thereof.

11. The process of Claim 10 wherein the diluent is used in an amount that is greater than 10 mole percent and less than 90 mole percent, based on the total moles of reactant hydrocarbon and diluent.

12. The process of any one of Claims 1 to 11 wherein the rare earth halide has a BET surface area greater than 3 m^2/g.

13. The process of any one of Claims 1 to 12 wherein the rare earth halide is represented by the formula MX_3, wherein M is at least one rare earth element selected from the group consisting of lanthanum, cerium, neodymium, praseodymium, dysprosium, samarium, yttrium, gadolinium, erbium, ytterbium, holmium, terbium, europium, thulium, lutetium, and mixtures thereof; and wherein X is chloride, bromide, or iodide.

14. The process of Claim 13 wherein M is lanthanum or lanthanum in a mixture of other rare earth elements, and X is chloride.

15. The process of any one of Claims 1 to 14 wherein the rare earth oxyhalide support has a BET surface area greater than 12 m^2/g.

16. The process of any one of Claims 1 to 15 wherein the rare earth oxyhalide support is represented by the formula MOX, wherein M is at least one rare earth selected from the group consisting of lanthanum, cerium, neodymium, praseodymium, dysprosium, samarium, yttrium, gadolinium, erbium, ytterbium, holmium, terbium, europium, thulium, lutetium, and mixtures thereof; and wherein X is chloride, bromide, or iodide.

17. The process of Claim 16 wherein M is lanthanum or lanthanum in a mixture with other rare earth elements, and X is chloride.

18. The process of any one of Claims 1 to 17 wherein the catalyst is bonded to or extruded with a support.

19. The process of any one of Claims 1 to 18 wherein the process is conducted at a temperature greater than 200°C and less than 600°C.

20. The process of any one of Claims 1 to 19 wherein the process is conducted at a pressure equal to or greater than 14 psia (97 kPa) and less than 150 psia (1,034 kPa).

21. The process of any one of Claims 1 to 20 wherein the process is conducted at a weight hourly space velocity of total feed, comprising the reactant hydrocarbon, the source of halogen, the optional source of oxygen, and an optional diluent, of greater than 0.1 h^{-1} and less than 100 h^{-1}.

22. A process of oxidatively monohalogenating methane to form methyl chloride or methyl bromide, the process comprising contacting methane with hydrogen chloride or hydrogen bromide, and oxygen in the presence of a catalyst at a temperature greater than 300°C and less than 500°C such that methyl chloride or methyl bromide is formed, the catalyst comprising a rare earth chloride or rare earth oxychloride compound that is essentially free of iron and copper, with the proviso that when cerium is present in the catalyst, then at least one rare earth element is also present in the catalyst.

23. The process of Claim 22 wherein the rare earth is lanthanum or lanthanum in a mixture with other rare earth elements.

24. The process of Claim 22 or 23 wherein the selectivity to methyl chloride or methyl bromide is greater than 60 mole percent.

25. A process of preparing methyl alcohol comprising (a) contacting methane with a source of halogen, and optionally, a source of oxygen in the presence of a catalyst under oxidative monohalogenation process conditions sufficient to prepare methyl halide, the catalyst comprising a rare earth halide or rare earth oxyhalide essentially free of iron and copper, with the proviso that when the catalyst contains cerium, the catalyst also contains at least one other rare earth element; and thereafter (b)

contacting the methyl halide thus prepared with water in the presence of a hydrolysis catalyst under conditions sufficient to prepare methyl alcohol and co-product hydrogen halide; and optionally (c) recycling the co-product hydrogen halide to the oxidative halogenation process step (a).

26. The process of Claim 25 wherein the source of halogen is hydrogen chloride, and oxygen is employed in process step (a).

27. The process of Claim 25 or 26 wherein the rare earth halide or rare earth oxyhalide is a rare earth chloride or a rare earth oxychloride.

28. The process of any one of Claims 25 to 27 wherein the rare earth is lanthanum or lanthanum in a mixture with other rare earth elements.

29. The process of any one of Claims 25 to 28 wherein the hydrolysis catalyst is selected from the group consisting of alumina, zeolites of the ZSM structure code, alkali and alkaline earth metal hydroxides and alkoxides, alkyl ammonium hydroxides, amines, halide complexes of platinum, palladium, and nickel, and metal oxides and hydroxides of Group IIA and the transition elements supported on γ-alumina or activated carbon.

30. The process of any one of Claims 25 to 29 wherein in step (b) the molar ratio of water to methyl halide is greater than 1:1 and less than 20:1.

31. The process of any one of Claims 25 to 30 wherein in step (b), the hydrolysis is conducted at a temperature greater than 85°C and less than 600°C, and at a pressure greater than 7 psia (50 kPa) and less than 725 psia (4,999 kPa).

32. A process of condensing methyl halide to form light olefins and/or gasolines comprising (a) contacting methane with a source of halogen, and optionally, a source of oxygen in the presence of a catalyst under oxidative halogenation process conditions sufficient to prepare methyl halide and, optionally, dihalomethane, the catalyst comprising a rare earth halide or rare earth oxyhalide being essentially free of iron and copper, with the proviso that when the catalyst contains cerium, the catalyst also contains at least one other rare earth element; and thereafter (b) contacting the methyl halide and, optionally, dihalomethane thus prepared with a condensation catalyst under conditions sufficient to prepare at least one light olefin, at least one C5+ gasoline,

or a combination thereof; and (c) optionally recycling the co-product hydrogen halide to the oxidative halogenation step (a).

33. The process of Claim 32 wherein the source of halogen is hydrogen chloride, and oxygen is employed in process step (a).

34. The process of Claim 32 or 33 wherein oxygen is provided as essentially pure oxygen or as air.

35. The process of any one of Claims 32 to 24 wherein the rare earth halide or rare earth oxyhalide is a rare earth chloride or rare earth oxychloride.

36. The process of any one of Claims 32 to 35wherein the rare earth is lanthanum or lanthanum in a mixture with other rare earth elements.

37. The process of any one of Claims 32 to 36 wherein the condensation catalyst is selected from the group consisting of aluminosilicates of the DCM-2 and ZSM structure codes, aluminophosphates, borosilicates, silicates, and silicoaluminophosphates.

38. The process of any one of Claims 32 to 38 wherein the process temperature is greater than 250°C and less than 600°C, and wherein the process pressure is greater than 0.1 psi absolute (689 Pa) and less than 300 psi absolute (2,068 kPa).

39. A process of preparing vinyl halide monomer comprising (a) contacting methane with a first source of halogen, and optionally, a first source of oxygen in the presence of a first oxidative halogenation catalyst under process conditions sufficient to prepare methyl halide and, optionally, dihalomethane, the catalyst comprising a rare earth halide or rare earth oxyhalide being essentially free of iron and copper, with the proviso that when the catalyst contains cerium, the catalyst also contains at least one other rare earth element; (b) contacting the methyl halide and, optionally, dihalomethane thus prepared with a condensation catalyst under condensation conditions sufficient to prepare ethylene and co-product hydrogen halide; (c) contacting ethylene with a second source of halogen, and optionally, a second source of oxygen in the presence of a second oxidative halogenation catalyst under oxidative halogenation process conditions, and optional thermal cracking conditions, sufficient to

prepare vinyl halide monomer; and optionally (d) recycling the co-product hydrogen halide to process steps (a) and/or (c).

40. The process of Claim 39 wherein the first and second sources of halogen are both hydrogen chloride, and oxygen is employed in process steps (a) and (c).

41. The process of Claim 39 or 40 wherein the first and second sources of oxygen are provided as essentially pure oxygen, or air, or oxygen-enriched air.

42. The process of any one of Claims 39 to 41 wherein in step (a) the rare earth halide or rare earth oxyhalide is a rare earth chloride or rare earth oxychloride.

43. The process of any one of Claims 39 to 42 wherein the rare earth is lanthanum or lanthanum in a mixture with other rare earth elements.

44. The process of any one of Claims 39 to 43 wherein the condensation catalyst is selected from the group consisting of aluminosilicates of the DCM-2 and ZSM structure codes, aluminophosphates, borosilicates, silicates, and silicoaluminophosphates.

45. The process of any one of Claims 39 to 44 wherein the condensation process temperature is greater than 250°C and less than 600°C, and wherein the condensation process pressure is greater than 0.1 psi absolute (689 Pa) and less than 300 psi absolute (2,068 kPa).

46. The process of any one of Claims 39 to 45 wherein in step (c) the second oxidative halogenation catalyst comprises a rare earth halide or rare earth oxyhalide being essentially free of iron and copper, with the proviso that when the catalyst contains cerium, the catalyst also contains at least one other rare earth element.

47. The process of any one of Claims 39 to 46 wherein ethylene from step (b) and methane are co-fed to the oxidative halogenation reactor of step (a) to produce a mixture of methyl halide and vinyl halide, thereby combining steps (a) and (c) in one reactor.

48. The process of any one of Claims 39 to 47 wherein the mixture of methyl halide and vinyl halide are separated; vinyl halide is collected as a product; and the methyl halide is recycled to step (b) to produce ethylene.

49. A process of preparing acetic acid comprising (a) contacting methane with a source of halogen and, optionally, a source of oxygen in the presence of an oxidative halogenation catalyst under oxidative halogenation process conditions sufficient to prepare methyl halide, (b) contacting the methyl halide thus produced with a source of carbonyl in the presence of a carbonylation catalyst under carbonylation process conditions sufficient to prepared acetyl halide; and thereafter (c) hydrolyzing the acetyl halide thus produced to yield acetic acid.

50. The process of Claim 49 wherein the oxidative halogenation catalyst is a rare earth halide or rare earth oxyhalide, being essentially free of copper and iron, and with the proviso that when cerium is present in the catalyst, at least one other rare earth element is also present in the catalyst.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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(54) Title: OXIDATIVE HALOGENATION OF C_1 HYDROCARBONS TO HALOGENATED C_1 HYDROCARBONS AND INTEGRATED PROCESSES RELATED THERETO

(57) Abstract: An oxidative halogenation process involving contacting a reactant hydrocarbon selected from methane, a halogenated C_1 hydrocarbon, or a mixture thereof with a source of halogen and, preferably, a source of oxygen in the presence of a rare earth halide or rare earth oxyhalide catalyst, so as to form a halogenated C_1 hydrocarbon having a greater number of halogen substituents as compared with the reactant hydrocarbon. Preferably, the product is a monohalogenated methane, more preferably, methyl chloride. The oxidative halogenation process to form methyl halide can be integrated with downstream processes to produce valuable commodity chemicals, for example, methyl alcohol and/or dimethyl ether; light olefins, including ethylene, propylene, and butenes; higher hydrocarbons, including gasolines; vinyl halide monomer, and acetic acid. Hydrogen halide, which is a co-product of these downstream processes, can be recycled to the oxidative halogenation process.

INTERNATIONAL SEARCH REPORT

tional Application No
PCT/US 02/11778

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C17/154 C07C17/10 C07C17/158 C07C21/06 C07C17/156
C07C29/124 C07C1/26 C07C51/54 C07C51/04 C10G50/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 228 799 B1 (AUBERT ET AL) 8 May 2001 (2001-05-08) column 1, line 56 - line 62 column 6, line 40 - line 52 ---	1
A	WO 83 00859 A (OLAH GEORGE A) 17 March 1983 (1983-03-17) claims ---	25
A	US 4 769 504 A (NOCETI ET AL) 6 September 1988 (1988-09-06) cited in the application claims ---	32
A	US 4 737 594 A (OLAH) 12 April 1988 (1988-04-12) cited in the application claims ---	39

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 September 2002	16-01. 2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	VAN GEYT, J

INTERNATIONAL SEARCH REPORT

ıational Application No
PCT/US 02/11778

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	WO 01 38271 A (THE DOW CHEMICAL COMPANY) 31 May 2001 (2001-05-31) claims	1

INTERNATIONAL SEARCH REPORT

....ternational application No.
PCT/US 02/11778

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-48

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-48

   Process for the oxidative halogenation of methane and processes for preparing methyl alcohol, olefins, gasoline and vinyl halide in whih the first step is the said oxidative halogenation step

2. Claims: 49-50

   Process for preparing acetic acid from methane

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 02/11778

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6228799 B	08-05-2001	FR 2748740 A	21-11-1997
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